



## Specification

A CVD apparatus using heating element and a method for removing a deposited film

### Background of the Invention

#### 5 Field of the invention

This invention relates to a CVD apparatus for forming a film by using a heating element set at a prescribed temperature and a method for removing a deposited film, and particularly to a CVD apparatus using heating element which an in-situ cleaning is applied to and its cleaning method.

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#### Description of the Invention

In the manufacturing process of semiconductor devices such as an LSI (large scale integrated circuit), display devices such as an LCD (liquid crystal display) and the like, a chemical vapor deposition (CVD) method is widely used for forming a variety of thin films on a substrate.

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As such a CVD method, a plasma CVD method which utilizes a plasma to decomposes and/or activate a material gas to form a film on a substrate and a thermal CVD method which utilizes the heat of a substrate to cause a reaction of a material gas and form a film on a substrate are well known. In addition to these methods, there is another CVD method in which a material gas is decomposed and/or activated to form a film by a heating element set at a prescribed high temperature. This CVD method is called "a CVD method using heating element", hereinafter.

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A CVD apparatus to carry out this method is constructed in such that a heating element made of metal having a high melting point such as tungsten and a substrate are disposed in a processing vacuum chamber, and a material gas is introduced into the chamber while the heating element is maintained at a temperature of about 1000-1800°C. The material gas introduced in the chamber is decomposed and/or activated to generate activated species when passing

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over the surface of the heating element. The activated species reaches the substrate and forms a thin film on the surface of the substrate. Of such a CVD method using heating element, one using a wire as a heating element is referred as a Hot-Wire CVD method, and the one that is thought to be utilizing the catalytic reaction of a heating element in decomposition or activation process of the material gas is referred as a Catalytic-CVD (or Cat-CVD) method.

In the CVD method using heating element, the decomposition or activation reaction of the material gas occurs when the gas passes over the surface of the heating element. Therefore, the substrate temperature can be lowered as compared with a thermal CVD method in which such a reaction is caused to occur only by the heat of the substrate. And unlike a plasma CVD method, the substrate is free from the damages caused by plasma. For these reasons, the CVD method using heating element is expected as a promising film forming method of semiconductor devices and display devices of the next generation, which will have higher integration and higher functions.

As the film formation is made on a substrate, a film is also deposited on the inner structures of the film forming apparatus in any film forming method including CVD methods mentioned above. The film deposited on the inner structures peels off when it becomes thick, which produces particles. The particles thus produced may be incorporated in the film on the substrate or adhere to the surface of the film, which causes the defect in the device and reduces production yield of the device.

In order to avoid these problems, the deposited film on the inner structures should be periodically removed before peeling off in the repetition of film formation.

One method often used for preventing the generation of particles due to the peeling-off of the deposited film is to cover the inner surfaces of the apparatus with any sheets or members on which the films are to be deposited instead of on the inner surface and to periodically exchange these sheets or members. However, since the deposition takes place even inside the narrow gaps of inner structure or on the hidden side of the sheets or members in the case of, e.g., the

CVD apparatus. It is impossible to perfectly prevent the generation of particles.

In contrast, as a method for removing a film deposited inside the film forming chamber, there is a method called an in-situ cleaning method in which a cleaning gas is introduced into the chamber and is made to react with deposited films with the aid of energy of plasma or heat to generate gaseous substances which can be exhausted.

Since the in-situ cleaning method is carried out without exposing the inside of the chamber to the atmosphere, the continuous and stable production of thin films having a prescribed characteristic becomes available. In addition, since neither the exchange of the sheets or members nor the operation of exhausting the chamber from the atmospheric pressure to a prescribed pressure is necessary, the time for the cleaning process is remarkably shortened. Thus, this method has an advantage in the productivity.

Moreover, this method makes it possible to remove even the film deposited inside the narrow gaps and effectively suppress the generation of particles.

When the in-situ cleaning method is applied to a plasma CVD apparatus used for forming, for example, a silicon film or a silicon nitride film, a cleaning gas such as  $\text{NF}_3$ ,  $\text{CF}_4$  or  $\text{CCl}_4$  is introduced into the processing chamber and the plasma is generated at a proper time after the film formation is repeatedly carried out. The cleaning gas is decomposed and/or activated by the plasma to react with a deposited film. A silicon film is converted to silicon tetrafluoride ( $\text{SiF}_4$ ) or silicon tetrachloride ( $\text{SiCl}_4$ ) and a silicon nitride film is to  $\text{SiF}_4$  or  $\text{SiCl}_4$  and nitrogen ( $\text{N}_2$ ). Since these gaseous substances are to be exhausted, the deposited film, consequently, can be removed.

In contrast, when a cleaning gas such as  $\text{ClF}_3$  that is easily decomposed by heat is employed, plasma is not necessary. The deposited film can also be converted to gaseous substances merely by heating the chamber. However, the chamber must be heated above  $200^\circ\text{C}$  in order to obtain the practical removal rate, which may cause the degradation of vacuum seals and substantially lengthens the cleaning time because it takes long time to heat and cool the chamber.

As has been mentioned, the in-situ cleaning of the film forming chamber is  
very important process to stably and continuously form a film with prescribed  
characteristics. Therefore, the present inventor attempted to apply the in-situ  
cleaning method to a promising CVD apparatus using heating element and  
5 found that the conventional in-situ cleaning methods have a problem that a  
heating element made of metal having a high melting point reacts with the  
cleaning gas, and the wire becomes thin. That is, in this attempt, there were  
placed electrodes for the plasma generation in the processing chamber, the  
cleaning gas was introduced and then plasma is generated to carry out the  
10 cleaning. Although the deposited film could be removed, the heating element  
was also etched to decrease its diameter. As a result, the prescribed exothermic  
characteristics could not be obtained in the next film formation.

A  $\text{ClF}_3$  gas as a cleaning gas was introduced into the film forming chamber  
which was heated to  $200^\circ\text{C}$  by using a heater installed outside. The heating  
15 element similarly reacted with the cleaning gas and was decreased in its  
diameter.

Thus, conventional in-situ cleaning methods cannot be directly applied to a  
CVD apparatus using heating element. However, since the in-situ cleaning is  
inevitable for continuous and stable production of films, further examinations on  
20 the structure of the CVD apparatus using heating element and the cleaning  
condition were made to establish the in-situ cleaning technology applicable to  
the CVD apparatus using heating element.

### Summary of the Invention

25 This invention has been completed for the first time based on the  
above-mentioned knowledge and discovery. The purpose of this invention is to  
provide a method for efficiently and completely removing a film deposited even  
on the surface of a member having a complicated shape without providing a  
heating means for heating the member.

30 In addition, the purpose of this invention is to provide an in-situ cleaning

method of a CVD apparatus using heating element which enables to remove a film deposited inside the apparatus without allowing the inside of the apparatus to expose to the atmosphere. Another purpose of this invention is to provide a CVD apparatus using heating element to which an in-situ cleaning is applied,

5 A method for removing a deposited film of this invention comprises a method for removing a film deposited inside a chamber which can be exhausted and/or on a member placed in said chamber, wherein after said chamber is exhausted, a heating element, at least the surface of which is composed of platinum, disposed in said vacuum chamber, is heated at a prescribed  
10 temperature and a cleaning gas which is decomposed and/or activated by said heating element to generate an activated species that converts said film into gaseous substance is introduced into said chamber

And said chamber is of a CVD apparatus which decomposes and/or activates a material gas by said heating element and deposits a film containing  
15 at least one element of said material gas on a substrate.

By making the surface of a heating element with platinum, it becomes possible to substantially prevent the reaction of the cleaning gas with the heating element and therefore the decrease in, e.g., the diameter of the heating element. Moreover, a heating element is made of platinum at least its surface, which  
20 makes it possible to efficiently decompose and/or activate the cleaning gas to generate activated species at a relatively low temperature and to effectively remove films deposited inside the chamber. And the activated species thus generated seems to have such a long lifetime that even films deposited on a complicated shape or the inside of the pipe can be removed. In addition, the  
25 in-situ cleaning which is inevitable for the continuous formation of films with high characteristics can be applied to a CVD apparatus using heating element.

This invention is also characterized in that at least a part of the surface of the inner structure of said chamber is covered with platinum.

The inner structures except for the heating element are corroded and  
30 etched by the cleaning gas. However, the corrosion of the inner structures does not influence the film forming performance or the removal performance of

deposit d films since these structures are generally very thick compared with a heating element. Nevertheless, if the performance of the inner structures such as a measurement element, a sensor and the like is deteriorated by the contact of the cleaning gas, it is desirable to cover the part with platinum to cut off the contact with the cleaning gas. A current lead member, for example, may also be covered with platinum when thin rod is used therefore.

In this invention, said cleaning gas comprises fluorine ( $F_2$ ), chlorine ( $Cl_2$ ), nitrogen trifluoride ( $NF_3$ ), carbon tetrafluoride ( $CF_4$ ), hexafluoroethane ( $C_2F_6$ ), octafluoropropane ( $C_3F_8$ ), carbon tetrachloride ( $CCl_4$ ), pentafluorochloroethane ( $C_2ClF_5$ ), trifluorochlorine ( $ClF_3$ ), trifluorochloromethane ( $CClF_3$ ), or sulfur hexafluoride ( $SF_6$ ).

These gases are sufficiently decomposed and/or activated with the aid of a heating element set at a prescribed temperature, and convert the deposited films to gaseous substances, resulting in efficiently removing the deposited film.

A CVD apparatus of this invention comprises a CVD apparatus using heating element for forming a film containing at least one element of a material gas on a substrate, composed of a process chamber able to be exhausted, an inlet of said material gas, and a heating element able to be set at a prescribed temperature disposed in said chamber, said material gas decomposed and/or activated by said heating element, wherein at least the surface of said heating element is composed of platinum and a gas supply system of a cleaning gas which is decomposed and/or activated by said heating element to generate activated species which converts a film deposited inside said chamber to gaseous substance, is provided so as to remove said deposited film without exposing the inside of said chamber to the atmosphere.

In this invention, the heating element is fabricated not to react with a cleaning gas. This makes it possible to carry out the cleaning only by introducing the cleaning gas and heating said heating element after film formations. Accordingly, an in-situ cleaning of the apparatus can be realized.

An electrode for plasma generation may be disposed in said chamber. Since the heating element will not react with a cleaning gas or plasma, a

conventional plasma cleaning method can be employed. Moreover, in the decomposition or activation of the gas, both the plasma and the heat of the heating element may be simultaneously employed. This increases the degree of freedom of the film formation and cleaning conditions, and therefore contributes to further improvements of film characteristics and cleaning efficiency.

### Brief Description of the Drawings

Fig.1 is a conceptual diagram showing a configuration example of a film forming apparatus employing a CVD method using heating element, which an in-situ cleaning is applied to.

Fig.2 is a conceptual plan view showing a configuration of heating element 3 shown in Fig. 1.

Fig. 3 is a sectional view of heating element 3 taken along the a-a' line.

### Detailed Description of the Preferred Embodiments

The preferred embodiments of this invention will be described below by referring to the accompanying drawings.

Fig.1 is a conceptual diagram showing a structural example of a CVD apparatus using heating element, which an in-situ cleaning method can be applied to.

A film forming apparatus shown in Fig.1 is composed of a processing vacuum chamber 1, an exhaust system 11 for exhausting the processing vacuum chamber 1, gas supplying systems 23,25 for supplying a material gas for the film formation and a cleaning gas, and a gate valve 5 through which a substrate is transferred. In processing vacuum chamber 1, a gas supply vessel 2 connected with gas supply system 23,25, a substrate holder 4, and a heating element 3, the surface of which is made of platinum, are installed.

The introduction of a material gas and a cleaning gas to gas supply vessel 2 is switched by valves 22,24. The feed rate of these gases is controlled by a

respective flow controller (not illustrated) provided in each of gas supply systems 23, 25. Gas supply vessel 2 has a hollow structure and a plurality of gas outlets 210 in the plane that faces to substrate holder 4. The exhaust systems 11 are connected to processing vacuum chamber 1 through a main valve 12 having an exhaust speed regulation function by which the pressure inside the processing chamber is controlled.

A support member 31 holds heating element 3 that is connected to an energy supply mechanism 30 for controlling the temperature of heating element 3. As an energy supply mechanism, a DC or AC power source is, in general, employed. The heating element is heated and maintained at a prescribed temperature by an electric current to decompose and/or activate a material gas during a film formation process and a cleaning gas during a cleaning process, which efficiently brings about the film formation and the cleaning.

Fig.2 is a conceptual plan view showing a configuration of heating element 3 shown in Fig. 1. In this case, heating element 3 is fabricated with a wire member formed in saw tooth shape and is held by a support member 31.

The heating element that has a platinum layer on the surface of a substrate member is described in detail by referring to Fig.3. Fig. 3 is a sectional view of heating element 3 taken along the a-a' line of Fig.2.

As shown in Fig.3, the heating element comprises a substrate member 301 and a coating layer 302 formed thereon. There is no particular restriction on the material of the substrate member, but the material which has a higher melting point than platinum is preferably employed such as tungsten, tantalum, niobium, carbon, iridium, molybdenum or rhodium, silicon carbide, PBN (pyrolytic boron nitride), alumina and the like. The coating layer 302 of platinum is formed by a method of electron-beam evaporation, sputtering, plating, lining or the like.

It is also possible to make whole heating element with platinum.

Next, the method of the film formation and the cleaning will be explained by using the apparatus shown in Fig.1.

#### (Film formation)

Firstly, a substrate is transferred into processing vacuum chamber 1



through gate valve 5 from a load lock chamber (not illustrated) and is placed on  
substrate holder 4. After processing vacuum chamber 1 is evacuated to a  
prescribed pressure by exhaust system 11, energy is supplied to heating  
element 3 from a DC or AC power source as an energy supply mechanism 30 to  
5 maintain heating element at a prescribed temperature. This temperature is  
usually determined, depending on the type of a film to be formed and a material  
gas; for example, a temperature around 1000°C is used for forming a silicon film  
with silane (SiH<sub>4</sub>) and hydrogen (H<sub>2</sub>).

Then, valve 22 is opened and the material gas is introduced into the  
10 processing vacuum chamber at a prescribed flow rate. The pressure inside the  
processing vacuum chamber is set at a prescribed pressure by the exhaust  
speed regulation function of main valve 12.

The material gas supplied into gas supply vessel 2 is blown off through gas  
outlets 210 in the direction of heating element 3, and is decomposed and/or  
15 activated by the catalytic action of platinum of the heating element maintained at  
a high temperature to generate activated species. The activated species  
reaches the substrate and the film is deposited on it. When the thickness of the  
film on the substrate comes to a predetermined value, the material gas and the  
energy to the heating element is cut off. After the chamber is evacuated, the  
20 substrate is carried to the load lock chamber through gate valve 5 to finish the  
film formation.

#### (Cleaning)

The repetitions of the film formation mentioned above also make the film  
deposited on the inner surface of the processing vacuum chamber, the substrate  
25 holder, the gas supply vessel, the support member and the like. When this  
deposited film is thickened, it will peel off to produce particles. The particles may  
be entrapped in the film during the film formation or may adhere to the surface of  
the film, which deteriorates the characteristics of the film or causes the defect in  
devices. Therefore, the following cleaning treatment should be made before the  
30 film becomes so thick to peel off and produce particles. The film thickness of a  
deposited film may be monitored with the aid of an optical sensor or be

estimated from the total film forming time.

In the cleaning process, the processing vacuum chamber is vacuated by fully opening valve 12, and the heating element is heated up to a prescribed temperature and maintained at the temperature by the DC or AC power source 30. Next, valve 24 is opened and the cleaning gas is introduced into processing vacuum chamber 1. The pressure is set at a prescribed pressure by main valve 12.

The gas ejected from gas outlets 210 is effectively decomposed and/or activated by the platinum of the heating element maintained at the high temperature to generate activated species. For example, the heating element is preferably heated at 400°C and 1000°C or higher in the case of employing  $\text{NF}_3$  and  $\text{CF}_4$  as a cleaning gas, respectively, and the activated species highly reactive with a deposited film is generated by the catalytic action of platinum. The platinum is stable against the activated species; therefore, the stable film formation can be carried out even after the cleaning treatment. The activated species reacts with the films deposited on the surface of the inner wall, the substrate holder and the like and converts them into gaseous substances. The films are gradually removed as the gaseous substances thus generated are evacuated outside by the exhaust system.

This condition is maintained until the deposited films are completely removed. Thereafter, the supply of the cleaning gas and the energy to the heating element is stopped, and the processing vacuum chamber is evacuated. The cleaning process is completed in this way.

The cleaning procedure in this embodiment is an example of the cleaning method of this invention. The main point of this invention is to carry out the cleaning in such that a cleaning gas is introduced while the heating element is heated by introducing an electric current. Therefore, for example, any procedure or order of the valve operation and the pressure adjustment with valves 22, 24 and main valve 12 different from those mentioned in the embodiment can also be adopted, or a dummy substrate may be placed on substrate holder 4 in the cleaning process.

In addition, although the gas is introduced into the chamber through gas supply vessel 2 in Fig.1, the cleaning gas can be introduced through different route from that of a material gas or can be introduced through a nozzle.

The heating element can also be placed at the different position from that shown in Fig.1, for example, inside the gas supply vessel.

Although the temperature of the objects to be treated such as the inner wall of processing chamber 1, substrate holder 4, and gas supply vessel 2 has not been mentioned in the embodiment, the objects may be heated by a heater to increase the removal rate of deposited films and shorten the cleaning time, since the higher the temperature of the objects the larger the reaction rate of the cleaning gas with deposited films.

On the other hand, deposited films can be removed without heating in such a short time as previously mentioned that whether the objects are heated or not is a matter of choice of the cleaning condition.

Moreover, in the conventional method using a gas such as  $\text{ClF}_3$ , a processing vacuum chamber must be heated in order to obtain practical removal rate of deposited films; however the heating treatment is not necessary in this invention as mentioned above, so that the time for heating and cooling the processing vacuum chamber which usually needs a long time can be omitted and therefore the substantial cleaning time can be remarkably shortened.

Heating element 3 is usually connected and fixed to current lead members (not illustrated) installed in the processing vacuum chamber. The current lead members are usually made of Mo or Cu and formed in rod or block shape. The electric current is applied to the heating element through current lead members from energy supply mechanism 30. The members react with the cleaning gas and are etched. However, this reaction will not influence at all the exothermic characteristic of the heating element since their cross sections are very large compared with that of the heating element.

Nevertheless, it may be possible to cover the surface of the current lead members with platinum to prevent the reaction with the cleaning gas. In this case, the coating of the platinum is made by a method of electron-beam evaporation,

sputtering, plating, lining or the like in the same way as that used for a heating element.

The in-situ cleaning method of a CVD apparatus using heating element has been described so far. The cleaning method of this invention is also available in the case of removing films deposited in other processing apparatuses or films deposited on various members. Here, the members are meant to include a measuring instrument, a sensor, a valve and the like usually used in vacuum apparatuses.

Films adhered to the inside of a vacuum vessel, for example, are removed in the following way. A heating element, at least the surface of which is made of platinum, is installed in the vacuum vessel so that the element can be heated from outside. A cleaning gas inlet port is also provided to the vacuum vessel. A deposited film can be removed by heating the element to a prescribed temperature and introducing the cleaning gas into the vacuum vessel.

In the case of removing films deposited on members, the members are placed in such a vacuum vessel, and similar treatment is carried out. In the case of pipe with a considerable length, a heating element is placed at the upstream of the pipe so that the gas is made flow inside the pipe. It is also possible to construct a vacuum vessel with pipes or members to be treated.

Even films deposited in narrow gaps of a member with complicated shape or inside the pipe can be effectively removed by this invention as has been mentioned. This seems to be attributed to the activated species of cleaning gas that is generated to be very reactive and have a considerably long lifetime by heating element made of platinum.

The removal method of the deposited film of this invention can be applied to various types of deposited films by appropriately selecting a cleaning gas and a cleaning condition. For example, when a cleaning gas containing fluorine or chlorine are used, various types of deposited films including metal films such as W, Ta and Ti can also be removed as well as semiconductors or insulators such as silicon, silicon carbide, and silicon nitride.

A cleaning gas is also selected according to the type of deposited film, the

cleaning condition, or materials of the processing vacuum chamber. A fluorine- or chlorine-containing gas is suitably used. In particular,  $\text{NF}_3$ ,  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ ,  $\text{CCl}_4$ ,  $\text{C}_2\text{ClF}_5$ ,  $\text{ClF}_3$ ,  $\text{CClF}_3$  or  $\text{SF}_6$  is preferably used. The gas can be diluted by, e.g., Ar or He or be mixed for practical use.

5 A heating element is used in a variety of shapes such as wire, rod, tube, plate, foil or the like. A wire may be further formed into coil or saw tooth shape. 41

In a CVD apparatus using heating element of this invention, an electrode for plasma generation can be disposed inside the processing vacuum chamber. That is, the plasma discharge of fluorine- or chlorine-containing cleaning gas is made to occur in the cleaning process instead of that the heating element is heated by an electric current. The cleaning gas is decomposed and/or activated by the plasma, enabling to remove a film deposited inside the processing chamber. And it is confirmed that the heating element of this invention does not practically react with plasma. Accordingly, an in-situ cleaning using plasma becomes available, in which the processing chamber needs not to be exposed to the atmosphere at the cleaning. 42

In addition, both the heating of the heating element and the plasma generation can be carried out at the same time in the film formation process and the cleaning process. The interaction of the heat by the heating element and the plasma further improves the film characteristics and the cleaning efficiency. 43

In the case of using  $\text{ClF}_3$  as a cleaning gas and heating a processing chamber or a member to decompose the gas, an in-situ cleaning is also available so long as materials of the chamber or member to be treated permit since the heating element is stable against the  $\text{ClF}_3$ . 44

25 (Application to the Industry)

The present invention makes it possible to provide a method for effectively removing films deposited inside various film forming chambers and on the members by heating a heating element made of platinum at the surface to a prescribed temperature, and introducing a cleaning gas.

30 In addition, a CVD apparatus using heating element which an in-situ cleaning is applied to is realized. As a result, a continuous production of thin

films having high characteristics become available by a CVD method using heating element which is expected as a promising manufacturing means of high characteristic films.

Thus, the present invention contributes to further improvement of the  
5 characteristics and productivity of semiconductor devices and display devices,  
and also promotes their development.